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PRACTICAL EXERCISES

IN

ELECTROCHEMISTRY

BY

DR. FELIX OETTEL

TRANSLATED
(WITH THE AUTHOR'S SANCTION)
BY

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Twenty Illustrations

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PREFACE.

Students of chemistry have been, from time to time, favored with special works relating to the preparation of typical compounds in inorganic and organic chemistry, as well as with guides outlining the more common methods of procedure in physical chemistry, in spectrum analysis, etc., and in them all they have found helpful suggestions which proved most valuable in the pursuit of their studies. In the present volume Dr. Oettel has aimed to present to the same student class the essentials of a course in practical electrochemistry. The examples given are not only simple, but they are also types of definite processes. They are not only instructive, but suggestive as well, and their careful study will be productive of most excellent results. That they may become more familiar to the chemical students of this country, where comparatively little attention has been paid to this highly interesting field of chemical research, has been the sole purpose in presenting this translation.

384324

CONTENTS.

GENERAL.

PAGE

Current Sources, ... 9
Regulators, ... 10
Measuring Apparatus, ... 11
Electrode Stands, ... 14
Voltameters, ... 15

I. TESTING AND CALIBRATION OF MEASURING APPARATUS, 19
1. Comparison between Silver and Copper Voltameters, 19
2. Control of Amperemeter with Oxyhydrogen Voltameter, ... 20
3. Testing of Amperemeter with Copper Voltameter, . . 22
4. Comparison of Amperemeter with Torsion Galvanometer, ... 24
5. Doubling Capacity of Amperemeter by Means of a Shunt, ... 25
6. Comparison of Voltmeter with Torsion Galvanometer, 27
7. Doubling Capacity of Voltmeter by Insertion of a Series Resistance, ... 29
8. Calibration of Galvanometer as Amperemeter, . . . 30
9. Calibration of Galvanometer as Voltmeter, ... 32

II. DEPENDENCE OF THE FALL OF BATH PRESSURE IN THE ELECTROLYTE UPON THE FACTORS: CURRENT DENSITY, CONCENTRATION AND TEMPERATURE OF SOLUTION, DISTANCE OF ELECTRODES FROM EACH OTHER, ... 35
10. Arrangement of Definite Current Strengths and Pressures, ... 35

PAGE
III. INFLUENCE OF CURRENT DENSITY AND CONCENTRATION ON THE COURSE OF ELECTROCHEMICAL REACTIONS, . . 38
11. Oxidation of Oxalic Acid, ... 40
12. Electrolysis of Mixed Ferrous and Ferric Solutions, . 41

IV. APPLICATION OF GAS ANALYSIS TO ELECTROCHEMICAL REACTIONS, ... 43
13. Formation of Hypochlorites and Chlorates, ... 43
14. Electrolysis of Hydrochloric Acid without a Diaphragm, ... 49

V. EXPERIMENTS WITH A DIAPHRAGM, ... 51
15. Electrolysis of Dilute Sulphuric Acid (or Sodium Hydrate) with a Diaphragm: Ion Transference, . . 51
16. Electrolysis of Salt with a Diaphragm, ... 52
17. Electrolysis of Hydrochloric Acid with a Diaphragm, 55
18. Formation of Persulphuric Acid from Sulphuric Acid by Electrolysis, ... 58

VI. METAL PRECIPITATIONS WITH SOLUBLE AND INSOLUBLE ANODES, ... 62
19. Copper Refining, ... 62
20. Copper Precipitation with Insoluble Anodes, ... 65

VII. INTRODUCTION OF AID-REACTIONS, ... 68
21. Experiments with Siemens' Copper Recovery Process, 68

VIII. EXPERIMENTS WITH MOLTEN ELECTROLYTES, ... 71
22. Preparation of Magnesium, ... 71
23. Electrolysis of Fused Lead Chloride, ... 74
24. Electrolytic Preparation of Alloys, ... 75

IX. EXPERIMENTS WITH MULTIPOLAR ELECTRODES, . . . 76
25. Copper Precipitation with Double-pole Electrodes, . 76
26. Electrolysis of Salt Solutions with a Mercury Kathode, 79

X. ORGANIC ELECTROLYSIS, ... 81
27. Electrolysis of Sodium Acetate, ... 81

PAGE
28. Reduction of Nitrobenzene to Azobenzene, ... 83
29. Preparation of Hydrazobenzene and Benzidine from Nitrobenzene, ... 85
30. Reduction of Nitrobenzene to p-Amidophenol, . . . 86
31. Preparation of p-Amidophenol-Sulphonic Acid from Nitrobenzene, ... 88
32. Oxidation of p-Nitrotoluene to p-Nitrobenzyl Alcohol, 90
33. Preparation of Iodoform, ... 91

PRACTICAL EXERCISES

IN

ELECTROCHEMISTRY.

SOURCES OF CURRENT.

The best sources of electric energy are storage cells. They may be directly charged by means of a small dynamo or from any direct current supply. In electrometallurgical investigations two accumulators with a pressure of four volts are generally all-sufficient, but in other electrochemical work a pressure twice as great is frequently necessary. This is especially the case in experiments involving gas analysis, where it is necessary to insert an oxyhydrogen voltameter in the circuit. In charging storage cells from the main line, a regulating resistance must be introduced in order to obtain the desired current strength. The current may be regulated so that the charging can take place over night without special oversight, and so that it may be finished on the return of the analyst in the morning.

To utilize the central station current to the best advantage in such cases, a large number of small storage cells, each of about fifty ampere-hours capacity, should be at the disposal of the analyst. These should be arranged in series during the charging, but on discharge they should be connected up in a group, giving a pressure of from four to eight volts.

As storage cells at the present time are so extensively used, a knowledge of the proper method of treating and handling them is presupposed. *

REGULATORS.

An adjustable rheostat with 15 to 20 contacts † is very convenient. It should be attached to the wall adjacent to the experiment table, and a resistance strip should be fixed to the edge of the table, with a total resistance equal to one division of the rheostat. Its purpose is to reduce the current to still smaller values. It will be found advantageous to run a conducting wire, in the shape of a flat metal strip, the entire length of the table. It should be slightly elevated, to protect it in case any one of the beaker glasses should break. By means of this wire it will be possible to make an attachment at any point along the table. A lead safety fuse of about five amperes

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* Compare K. Elbs, "Die Akkumulatoren," 2. Aufl., Leipzig, 1896.

† Voight u. Haeffner, Boeckenheim-Frankfurt a. M. Modell 131.

is introduced in front of the adjustable rheostat, so that in case of accident or carelessness the storage cells are not damaged. One pole of the battery is attached to the flat metallic strip, while the conducting wire from the other pole passes successively through the safety fuse, the rheostat, and the resistance band or strip, terminating in a binding post, with which the apparatus for the experiment is to be connected.

MEASURING APPARATUS.

The measuring instruments * (form E) devised by Meyer are very suitable for this purpose; although cheap, they are perfectly reliable. Their only disadvantage is the slight damping. When the instrument is inserted in the circuit, the index oscillates for some time about the zero-point, but this is of little moment, because in experimental work the measuring instruments are kept constantly in the circuit.

The instruments of Weston † are exceedingly accurate. The index in them assumes its position almost instantly, but they are much more expensive than the apparatus of Meyer. The spring amperemeters of Kohlrausch ‡ of the smaller types usually have high resistance and require too great a pressure for their operation.

---

* Dr. Paul Meyer, Berlin–Rummelsburg.

† Rich. C. Heinrich, Berlin, S. W., Ritterstrasse 88.

‡ Hartmann und Braun, Boeckenheim–Frankfurt a. M.

For purposes of instruction, convenience need not necessarily be considered, the object of the student being to *learn;* hence, the author feels justified in recommending instruments with a small range of graduation (amperemeters not exceeding three amperes, and voltmeters not exceeding five volts), so that, by introducing a shunt or a series resistance, the student may enlarge their capacity. The time consumed in overcoming these purely physical and mechanical conditions will be richly repaid by the practical knowledge which the operator gains of the nature of current and pressure measurement.

Just as the chemist must test his weights from time to time, so must the electrochemist test the accuracy of his measuring instruments. Instruments intended to measure strong currents or high pressures should be compared with a normal instrument. Formerly the torsion galvanometer of Siemens and Halske was almost exclusively used for this purpose; at present it is being rapidly superseded by normal Weston instruments.

The instruments thus far mentioned are not affected by currents in their neighborhood; indeed, they can be used in the vicinity of running dynamos, and hence are well suited for laboratory instruction. Instruments having magnetic needles have a more limited application. They can only be used at a considerable distance from dynamo machines, and should stand some meters away from main conducting wires.

A calibration table, for the place in which the instrument is set up, must be empirically determined. It is not transferable to any other locality, because in this new position there will probably be a different arrangement of the surrounding masses of iron (gas pipes, etc.), and hence other equilibrium conditions will prevail. Despite all these difficulties, the galvanometer possesses many conveniences. By means of shunts, which can be easily constructed, it may be used as an amperemeter for the most widely varying current strengths, and by the introduction of series resistances it may be calibrated as a voltmeter and applied to measure the most widely varying pressures. When, therefore, the local conditions are favorable, it is possible, with a galvanometer and a few shunt and series resistances, to replace a large number of amperemeters and voltmeters. It is also possible to select that combination which, for the case in hand, will afford the most accurate readings. In the opinion of Ostwald, Dr. Stöhrer & Son of Leipsic make a galvanometer suitable in every respect for all these purposes. Its price is about $10.00. The internal resistance of this instrument is about ten ohms. It has oil damping, the magnetic needle being provided with a vane dipping into oil. Any degree of damping may be obtained by diluting the rape-seed oil with petroleum.

The galvanometer, the shunt, and the series resistance are to be so connected with a commutator that by reversing the latter it is possible to pass directly from current measurement to pressure measurement (Fig. 1). The mercury cups 1 and 2 lead to the galvanometer, 3 and 4 to the shunt, while to 5 and 6 is attached the main conductor with the inserted series resistance as shown (see Fig. 2).

The galvanometer of Deprez-d'Arsonval is not influenced by neighboring currents, hence it may be used in any locality. It can be obtained from Hartmann and Braun, Boeckenheim; price, $25.00.

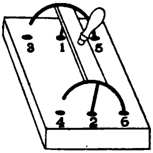

FIG. 1.

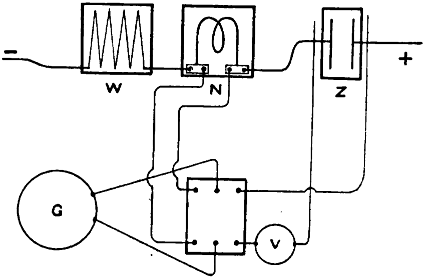

FIG. 2.

ELECTRODE STANDS.

The base of these stands should be rather broad and heavy, and in height they should be about 40 cm., so that it will not be necessary to raise the stands if heat is to be applied in the electrolysis. A very simple construction, used with advantage for years by the author, is pictured in Fig. 3.*

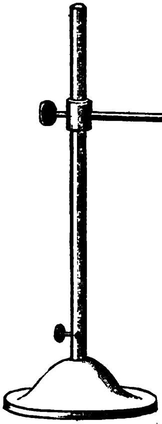

FIG. 3.

VOLTAMETERS.

Copper voltameters and oxyhydrogen voltameters deserve consideration. Both can be used for the calibration and control of amperemeters. They also answer for other purposes. Thus, the copper voltameter may be used as an ampere-hour meter by inserting it continuously in the circuit in quantitative experiments, and thereby ascertaining, from the weight of copper deposited, the quantity of current which has passed through the experimental system. The oxy-hydrogen voltameter is valuable in following the gas-analytical side of electrochemical reactions (Experiments 13 and 14).

---

* May be obtained from Haas and Stahl, Aue i. S.

Copper Voltameter.—The anode is a heavy plate of copper, while the kathode is a thin plate of the same metal. The latter should not extend to the bottom of the vessel. When working with heavy currents, an anode is placed on each side of the kathode. The vessels most suitable for this purpose are small glass troughs, but beaker glasses can be used. The electrodes should then have the form of concentric cylinders. The solution * should consist of 150 grams of copper sulphate, 50 grams of H_2SO_4, 50 grams of alcohol, and 1000 grams of H_2O. It can be used for some time. During use the liquid should be well mixed. This can be accomplished by a small agitator or stirrer, or by conducting a current of hydrogen through it. With experiments occupying a short time, it will be sufficient to stir the liquid with a glass rod. At the conclusion of the experiment wash the kathode with water, then rinse it with alcohol, and dry directly over a flame. When this instrument is used as a current meter, the weighing should be made with a good balance. The purpose of the amperemeter simultaneously inserted in the circuit is to indicate the current strength at any moment. It is also useful in regulating the current.

---

* Oettel, *Chem. Ztg.*, 1893, 543.

Oxyhydrogen Voltameter.—This voltameter is the most convenient instrument for the calibration and control of amperemeters. For this purpose the fall of pressure required by the instrument itself is not disturbing. It is only in gasometric investigations that it is inserted continuously in the circuit. The customary arrangement of the oxyhydrogen voltameter, with platinum electrodes in dilute sulphuric acid, gives accurate results only when all conditions leading to the formation of persulphuric acid or ozone are avoided.

The alkaline voltameter, with nickel electrodes, suggested by the writer, always yields accurate results. In consequence of the large electrode surface, the internal resistance is slight. The ordinary arrangement of this apparatus consists of a thick-walled glass cylinder with two concentric nickel plates. The conducting wires attached to these are also of nickel; they pass through rubber stoppers. The inner cylinder is always the anode. Through its stopper passes a glass tube, cut obliquely at its end. It serves to conduct out the gases and also to fill and empty the apparatus. The liquid used in this apparatus is sodium hydroxide (about 15 per cent. NaOH). It should not contain chlorine. As its volume is diminished by the decomposition of the water present, and also by evaporation, it is customary to make good the loss by adding water.

To the tube conducting out the gases is attached a long, narrow glass tube by means of short rubber tubing. It delivers the oxyhydrogen gas into the gasometer. The latter is a flask from which the bottom has been removed. Its capacity is about 150 c.c. It terminates in a capillary tube, usually closed with a piece of rubber and a glass rod. The gasometer is suspended in a flat pneumatic trough with overflow, so that the pressure in the voltameter can not change as the bell-jar fills with gas. The arrangement of this apparatus is shown in Fig. 4. After the current has begun to flow, the movable gas delivery tube is placed for a few minutes under the bell-jar. The collected gas is then conducted by means of the capillary tube into a Hempel apparatus, where it is measured (see Experiment 2).

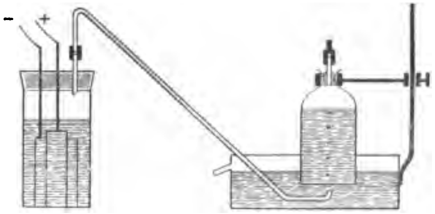

FIG. 4.

I. Testing and Calibration of Measuring Apparatus.

1. COMPARISON OF SILVER AND COPPER VOLTAMETERS.

The silver voltameter is universally recognized as the most accurate instrument of its class. To show that the copper voltameter, described on page 16, affords just as accurate results, perform the following experiment: Arrange in circuit (in series) a regulating resistance, a copper voltameter, and a silver voltameter. The latter consists of a beaker glass containing a neutral solution of silver nitrate (1 : 7). The anode is a plate of pure silver, while the kathode is a strip of platinum. A current of one ampere will precipitate 67.08 mg. of silver a minute. But as this metal shows a tendency to separate in a crystalline form, and does not adhere well to the kathode, strong currents should be used only for a short period, and, as soon as the silver appears inclined to fall off, the kathode should be again cleaned with nitric acid. Use currents of different density, and compare the quantities of copper precipitated with those calculated from the precipitated silver. On repeating the experiment, with the difference that the copper voltameter now contains the usual neutral and almost saturated copper sulphate solution, it may be easily demonstrated that, with current densities below 0.3 ampere for each square decimeter, the results will be too high. This is due to cuprous oxide present in the deposited metallic copper. Next, arrange for pressure measurements, and show that with equal current densities in the silver voltameter and in the neutral copper voltameter the pressure will be higher than if an acid-alcohol solution were used. It is, of course, hardly necessary to mention that the pressure measurements must not be conducted at times when quantitative experiments are being performed.

2. CONTROL OF AN AMPEREMETER WITH AN OXYHYDROGEN VOLTAMETER.

Arrange in series in the circuit: A regulating resistance (W), the amperemeter (A) to be tested,

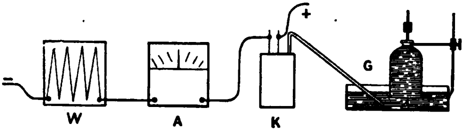

FIG. 5.

and the oxyhydrogen voltameter (K) (Fig. 5). The electrolytic gas evolved is collected under a bell-jar (G). When the desired current strength has been obtained by means of the regulating resistance, and the index of the amperemeter has come to rest, the delivery tube of the voltameter is placed under the bell-jar for a few minutes. To measure the volume of the collected gas, conduct it by means of the capillary tube into a Hempel gas burette. Read the volume of the gas after two minutes. The burette and liquid in the bell-jar (G) should previously have stood in the laboratory some time, in order to acquire the temperature of the surrounding air. Representing the volume of gas by v, the barometric pressure by *b*, and the pressure of the aqueous vapor by *h*, for the observed temperature *t*, the corrected volume of gas, v, will be found as follows:

$$V = V_1 \frac{(b-h)\ 273}{760\ (273 + t)}.$$

Generally, from 40 to 100 c.c. of gas are collected. With currents exceeding five amperes, the error arising in the time measurement is eliminated by taking the mean of several experiments. A current of one ampere yields 10.44 c.c. of electrolytic gas a minute (at 0° and 760 mm.). The desired current strength in amperes is, therefore:

$$i = \frac{V}{10.44}.$$ *

The current strengths are now accurately determined for a number of points on the amperemeter,

---

* For most purposes it suffices to divide the number of cubic centimeters of oxyhydrogen gas (measured at the temperature of the room) by 11, in order to get the amperes; that is:

$$i = \frac{V_1}{11}.$$

say for every half-ampere. These are then arranged in a table. If the instrument has never been calibrated, attach a provisional millimeter division to the scale; determine, as already indicated, the current strengths for a number of points, and from these values construct a curve, in such a manner that the millimeters represent the abscissas and the corresponding current strengths the ordinates. It will be evident from this curve at what points of the provisional scale the individual divisions for amperes, or fractions of amperes, are to be marked.

3. TESTING AN AMPEREMETER WITH A COPPER VOLTAMETER.

Arrange in series in the circuit: The regulating resistance (W), the amperemeter (A), and the copper voltameter (K) (Fig. 6). The electrodes in the copper voltameter are plates of sheet-copper, cut in such a manner that they can rest upon the edge of the retaining vessel. Two connected plates, about two mm. in thickness, serve as the anode; a thin plate,

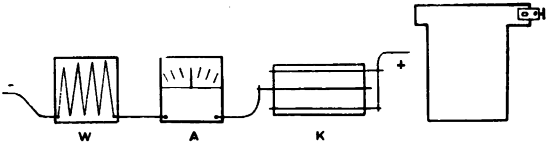

FIG. 6.

[illegible] to that of about 0.2 mm., of metal hanging betw[illegible] kathode. During use a moderately stro[illegible] hydrogen gas is passed through the volta[illegible] constantly mix the liquid. In all experiments kathodes of equal size are employed; one of thes[illegible] is used for the actual observations, while the other serves for the adjustment of the proper current strength. At the beginning of the experiment this kathode is suspended in the liquid, and, by aid of the regulating resistance, the desired position of the index of the amperemeter is obtained. When this point has been reached, interrupt the current and exchange the kathode strip for the first kathode, which has been accurately weighed; then close the circuit for several minutes. The quantity of copper deposited per ampere and per minute will be 0.0197 gram. Note the time occupied in the experiment, arranging it so that not less than 0.05 gram and not more than 0.2 gram of copper will be precipitated. When the liquid is kept well mixed, three amperes can be used for each square decimeter of the total kathode surface.

While the circuit is closed note the deflection of the amperemeter. Having determined from the weight of the copper precipitated the actual current strengths for a number of divisions of the instrument, arrange the results in a curve, and deduce from these a table of corrections.

N AMPEREMETER WITH A GALVANOMETER.

resistance W, the amperemeter A to the shunt N of the torsion galvan- re arranged in series, as in Fig. 7. The ometer is set as nearly as possible in the meridian. The arrest of the bell-magnet is carefully released and the instrument brought into a vertical position by the leveling screws, so that the brass point at the lower end of the magnet has free swing over the point of intersection of the cross marks. The galvanometer is now turned about its vertical axis until the index of the magnet stands over the zero point of the graduated circle, when it is again clamped, and the conducting wires are attached to the middle binding screws of N. On one branch is inserted the key T. The poles are so arranged that during the passage of the current the index of the

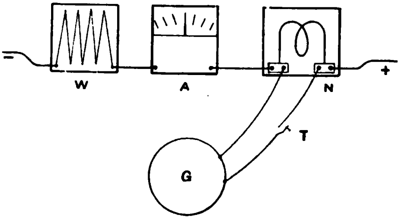

FIG. 7.

magnet is deflected in a direction *opposite* to that of the divisions on the torsion scale.

By means of the regulating resistance, varying current strengths are successively produced. The deflection of the amperemeter is read, the key T is pressed down, and the torsion head of the galvanometer is turned in the direction of the divisions until the indicator again stands over zero. If the resistance of the torsion galvanometer is one ohm, that of the shunt $\frac{1}{99}$ of an ohm, then every degree of the torsion angle will correspond to a current strength of 0.1 ampere.

It is advisable to test the readings of a torsion galvanometer at frequent intervals. This may be done by replacing the amperemeter in the above sketch by a silver or copper voltameter (compare pp. 16 and 17).

5. DOUBLING THE CAPACITY OF AN AMPEREMETER BY MEANS OF A SHUNT.

By arranging a shunt between the two points A and B of a circuit, it is possible to deviate or deflect any desired fraction of the current from its original path and conduct it through the shunt. The current strengths traversing the two branches are to each other inversely as the resistances, provided that no electromotive forces occur in these branches. Representing the resistances of the two branches by w_1 and

w_2, the main current I will divide itself into two components, $i_1 + i_2$, and—

$$i_1 = \frac{w_2}{w_1 + w_2} I$$

$$i_2 = \frac{w_1}{w_1 + w_2} I.$$

This law relating to the branching of the current is applied when using an amperemeter for current strengths higher than that for which it was constructed. To increase the capacity *n* times, attach a shunt whose resistance is $\frac{1}{n-1}$ of the resistance of the amperemeter. The readings of the instrument multiplied by *n* give the actual current strengths.

As example, let $n = 2$; then, to double the capacity, a shunt must be constructed with a resistance equal to that of the amperemeter. Suppose the latter to have been arranged for three amperes. Use nickelin wire of one mm. in thickness as material for the shunt, and for its measurement follow the arrangement pictured in Fig. 8.

R is a rheocord, the simplest form of a Wheatstone bridge; E, the source of the current, is either a primary battery or a storage-cell. S is a sliding contact, which is placed in the middle of the bridge wire. G is the galvanometer. The amperemeter A forms the third branch, while the nickelin wire N, as well as the stout copper wire K, constitutes the fourth branch of the bridge combination. The nickelin wire between the rheostat and the copper wire K is shortened or lengthened, until, upon pressing down the key T of the galvanometer, no further deflection is produced. This length of nickelin wire is then cut off, and, when soldered at its ends to two short copper wires, constitutes the desired shunt. For control purposes, several measurements of the current are now made with an oxyhydrogen voltameter. The deflection of the amperemeter obtained by the attachment of the shunt, when multiplied by two, must yield the current strengths obtained by the voltameter.

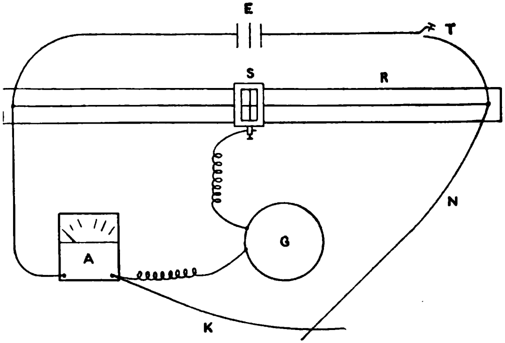

FIG. 8.

6. COMPARISON OF A VOLTMETER WITH A TORSION GALVANOMETER.

Attach to a narrow board, between the binding posts A and B, a nickelin wire 0.3 mm. in thickness and one meter in length. The arrangement is similar to that of a Wheatstone bridge. A battery E (Fig. 9), consisting of two or three storage-cells (when it is intended to measure four to six volts), is attached to the ends of the nickelin wire by means of a heavy copper wire. Attached to the wire is a sliding or movable contact S, from which, by means of key 1, connection is made with the torsion galvanometer T and the series resistance v. By the insertion of key 2 it is connected up with the voltmeter V which is to be tested. The other connections, both of the torsion galvanometer and of the voltmeter, are attached to the binding screw A.

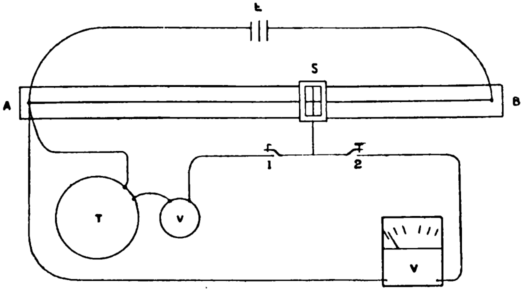

Fig. 9.

In carrying out the control measurements, close the battery circuit, press down upon key 2, and move the sliding contact along the board until the voltmeter indicates the first desired reading—*e. g.*, 0.5

volt. Liberate key 2, press down upon key 1, without changing the position of S, and carefully read the pressure indicated on the torsion galvanometer.

When the torsion screw has been turned again to zero, proceed to the next adjustment, and in this way determine the correct values for a definite number of divisions on the voltmeter by means of the torsion galvanometer.

7. DOUBLING THE CAPACITY OF A VOLTMETER BY THE INTRODUCTION OF A SERIES RESISTANCE.

It will frequently be necessary to measure higher pressures than the instrument at the disposal of the operator will permit. In such cases a series resistance will prove helpful. When a voltmeter is to be used for twice its capacity, only one-half the current ordinarily carried by it should pass through it. This can be accomplished by throwing in a resistance equal to that of the instrument, thereby increasing the total resistance of the combination to double what it was at first. If a resistance twice that of the voltmeter be inserted, then only one-third of the original current will pass through the system, and the actual pressures will consequently be three times that of the new readings, etc.

The experimenter should first ascertain the resistance of the voltmeter at his disposal. This is done in the usual manner, with a simple Wheatstone bridge and a known standard resistance. Let him next measure an equal resistance in the form of thin, covered nickelin wire (from 0.1 to 0.2 mm. in thickness), and wrap this wire upon a spool, soldering the two ends to heavy copper wires. The resistance thus constructed is placed in a glass bottle, the copper wires projecting through the stopper.

The pressures observed on the voltmeter when using this series resistance will be doubled. The arrangement of the apparatus is shown in Fig. 10. Z is the experimental cell, the pressure in which is to be measured.

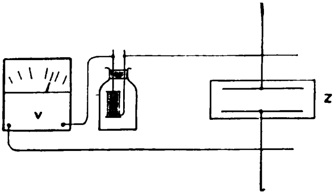

FIG. 10.

8. CALIBRATION OF A GALVANOMETER AS AN AMPEREMETER.

To adjust a galvanometer so that it may be used as an amperemeter, employ a shunt. It should always be inserted in the main current. It carries the major portion of the current, only a fraction of the latter passing through the galvanometer. The material for the shunt is either nickelin wire, 1 mm. in thickness, or copper wire, depending upon whether feeble or strong currents are to be used. The first thing to be done is to determine the length of the wire. To this end arrange in series in the circuit the apparatus, as shown in Fig. 11: the regulating resistance W, the shunt N, and the electrolytic voltameter K, together with the pneumatic trough. The highest current for which the instrument is to be calibrated is then conducted through the apparatus, and the points on the shunt wire (made straight for the purpose) are determined, to which the conducting wires of the galvanometer G must be attached in order to obtain a deflection of 60 degrees. (The measurements are untrustworthy when the readings exceed 60 degrees.) The

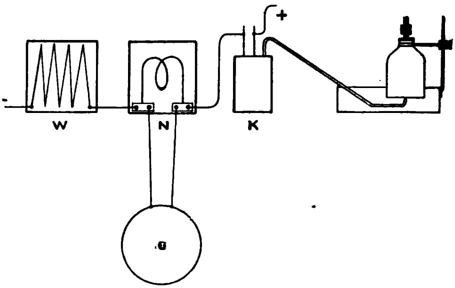

FIG. 11.

measured section of wire is cut off and its ends are soldered to copper strips provided with binding screws, by means of which it is attached to a board.

To calibrate the galvanometer, arrange a series of varying current strengths with the help of the regulating resistance. These are accurately measured by the use of an oxyhydrogen voltameter. At the same time the corresponding deflections of the galvanometer are noted. The numbers thus obtained are transferred to millimeter paper, the current strengths being made the abscissas and the corresponding deflections the ordinates. The points thus established are plotted in a curve, from which, reading backward, we can obtain the current strengths for all the deflections.

9. CALIBRATION OF A GALVANOMETER AS A VOLTMETER.

The galvanometer may be empirically calibrated as a pressure meter without much difficulty. It will be sufficiently accurate for all technical purposes. Storage cells are necessary to do this. The pressure of a cell of this kind, which has lost a fraction of its charge, may be assumed to have a voltage of two. If the accumulator circuit be closed by means of a thin wire of German silver, the pressure between its two ends will be two volts, while that between one end and the middle of the wire will be one volt, etc. If the wire is exactly one meter long, each centimeter of it will correspond to $\frac{1}{100}$ of the pressure at the ends.

In the case cited each centimeter will equal 0.02 of a volt. Therefore, it will be necessary only to connect the galvanometer by thin wires successively to those points of the German silver wire which represent 0.1, 0.2, 0.3, etc., volts, and to note the deflections, in order to use the instrument as a voltmeter graduated in tenths. To obtain suitable deflections of a galvanometer, the latter should be provided with a series resistance, the value of which is adjusted according to the pressure to be measured and the sensibility of the instrument. When the operator has a choice between a galvanometer with low sensibility provided with a low series resistance, and a delicate instrument which will necessitate the insertion of high resistance, the latter is preferable.

Experiment.—The galvanometer is to be used for four volts. The arrangement of the experiment is shown in Fig. 12. Two double binding posts, one meter apart, are screwed into a board. They are connected by a nickelin wire 0.3 mm. in thickness. Two storage-cells, arranged in series, are joined to them by means of heavy copper wires. It is very essential in closing the battery to use stout copper wire, whose resistance, as compared with the resistance of the German silver wire, may be entirely neglected; otherwise a fall of pressure, too considerable to be disregarded, will take place in the copper wires.

First, the magnitude of the series resistance must be determined. It is to be adjusted in such a manner that in determining the highest pressure which is to be measured (in this case four volts) there will result a deflection of 60 degrees. This is most conveniently accomplished by the use of a rheostat. From 400 to 700 ohms will be necessary, depending upon the sensibility of the instrument. The experiment may now be interrupted until this resistance has been constructed from thin, covered German silver wire (compare p. 32), after which the calibration is resumed. Connect one conducting wire of the galvanometer G permanently to one binding screw of the straight German silver wire. With the other conducting wire which contains the series resistance v, make contact with successive points of the German silver wire, advancing from 0.1 to 0.1 volt, that is, from 25 to 25 mm., and observe the deflections of the galvanometer.

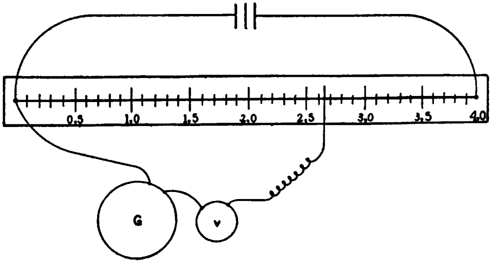

FIG. 12.

In this way a table of tenths of volts may be constructed.

By constructing a second resistance equal to the first plus the internal resistance of the galvanometer, it will be possible, without a new calibration, to use the instrument for eight volts. For its applicability, compare page 13.

II. Dependence of the Fall of Bath Pressure in the Electrolyte upon the Factors: Current Density, Concentration, and Temperature of Solution; Distance of Electrodes from Each Other.

10. ARRANGEMENT OF DEFINITE CURRENT STRENGTHS AND PRESSURES.

The experiments should be carried out in a rectangular glass vessel with electrodes 5 × 10 cm.; that is, one square decimeter total surface. On each side of the kathode is suspended an anode. Nickel (or iron) sheets are used when the electrolyte is sodium hydroxide. Sheet lead or platinum is substituted when sodium sulphate or sulphuric acid is the electrolyte. If but one side of the electrode is used, the pressure will be affected somewhat according as the electrodes fill up the section of the vessel more or less completely, since the reverse sides of the electrodes take part in the reaction. By means of the regulating resistance a series of current strengths is produced of 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 amperes. Note, at the same time, the pressure indicated by the voltmeter V (Fig. 13), which is continuously kept in the circuit. The experiments should be conducted with varying separation of the electrodes, with varying concentrations, and with varying temperatures. The result is a number of observations, of which two always give evidence of the influence exerted by electrode separation, or current density, or temperature, or concentration, upon the pressure, other conditions being the same. (It is possible to heat even a thick-walled glass receptacle without danger by the use of a water-bath, the bottom of which is covered with glass rods.)

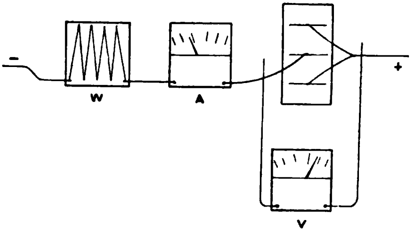

FIG. 13.

A review of the experiments may be given as follows:

A. Experiments in the Cold.

1. Three per cent. NaOH or Na_2SO_4.
   (*a*) 2 cm. electrode separation, 6 observations with 0.5–3.0 amperes.
   (*b*) 5 " " " 6 " " 0.5–3.0 "

2. Ten per cent. NaOH or Na_2SO_4.
   (*a*) 2 cm. electrode separation, 6 observations with 0.5–3.0 amperes.
   (*b*) 5 " " " 6 " " 0.5–3.0 "

B. Experiments aided by Heat (about 60°–70° C.).

3. Three per cent. NaOH or Na_2SO_4.
   (*a*) 2 cm. electrode separation, 6 observations with 0.5–3.0 amperes.
   (*b*) 5 " " " 6 " " 0.5–3.0 "
4. Ten per cent. NaOH or Na_2SO_4.
   (*a*) 2 cm. electrode separation, 6 observations with 0.5–3.0 "
   (*b*) 5 " " " 6 " " 0.5–3.0 "

The results may be arranged either in the form of a table or they may be plotted in curves. As the electrode surface is one square decimeter, the employed current strengths correspond to the current densities, 50, 100, 150, 200, 250, and 300 amperes per square meter.

CURRENT DENSITY PER SQUARE METER.	COLD.		HOT.					
	3 per cent.		10 per cent.		3 per cent.		10 per cent.	
	2 cm.	5 cm.	2 cm.	5 cm.	2 cm.	5 cm.	2 cm.	5 cm.
50 amperes, ...								
100 amperes, ...								
150 amperes, ...								
200 amperes, ...								
250 amperes, ...								
300 amperes, ...								

The graphic representation of results in curves is recommended. The curve enables the operator to examine a large series of results at a glance. The formation of an irregular line calls his attention to experimental errors, and enables him also to interpolate between the values directly determined. A series of curves can be best compared if they be transferred to tracing paper (drawn equally large and with the same variables as abscissas). They can then be so superposed that the co-ordinate axes cover each other. In the preceding case it is possible to learn from the curves what current strength will result if a prescribed, definite pressure exists in the electrolytic bath, and it will be noticed, too, that the most varying currents can exist according as the electrodes are more or less removed from each other, and according as the concentration and the temperature of the electrolyte are varied.

III. Influence of Current Density and Concentration upon the Course of Electrochemical Reactions.

Electrolytic reactions take place directly at the electrodes. Oxidation and reduction processes can therefore be approximately quantitative only when there is a sufficient quantity of the material to be oxidized or reduced in the vicinity of the electrodes in a given unit of time. This condition may be fulfilled by highly concentrating the solution or by low current density. Secondary reactions (usually decomposition of water) must occur in proportion as the choice of substances upon which the current acts is made more difficult, in consequence of the diminishing concentration of the material acted upon or of the high current density. Hence, it follows that—

Oxidation is most facilitated by concentrated solutions and by low current density at the anode.

Reduction is assisted by concentrated solutions and low current density at the kathode. Oxidation is less likely to occur in diluted solutions and with high current density at the anode. Dilute solution and high current density at the kathode are unfavorable to reduction. By a careful application of these conditions it is frequently possible to dispense with a diaphragm. Should it be possible for the substance which is reduced at the kathode to be re-oxidized at the anode, it may happen that the two active, opposing currents will neutralize each other. In such instances, in the same solution and with the same current density, we may obtain either an oxidation or a reduction, or even no effect at all, according to the electrode surface employed (Experiment 12). *A statement of the current density at both electrodes is, therefore, absolutely essential in reports upon electrochemical methods.*

11. OXIDATION OF OXALIC ACID.*

Arrange in series in the same circuit: the regulating resistance W, the amperemeter A, the copper voltameter K, and three cells I, II, III (Fig. 14). Beaker glass I contains 120 c.c. of a solution of 60 grams of oxalic acid and 50 grams of sulphuric acid in one liter of water. The anode is a cylinder of platinum about five cm. high and four cm. in diameter. The kathode is a spiral of platinum wire standing within the anode.

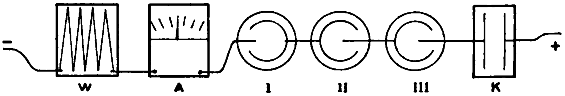

FIG. 14.

Beaker glass II contains a similar solution with similar electrodes, but with reversed polarity.

Beaker glass III contains electrodes of the same form and arrangement as II, but the electrolyte is 120 c.c. of a liquid of one-tenth the concentration of that in I and II. Hence, in I there is low current density at the anode, while in II and III the anode current density is high. The solution in I and II is concentrated, while that in III is dilute. A current of about 0.3 ampere is conducted through this combination for one hour; then it is interrupted. The precipitated copper is weighed. A definite portion of liquid is removed from each cell, and the residual oxalic acid, in each case, is determined with permanganate of potassium. In this way the oxalic acid oxidized in the three cells is ascertained. It will be found that the greatest oxidation has occurred in I and the least in III. From the reading of the copper voltameter, calculate what portion of the current was consumed in each case. Alter the experiment by working at a temperature of 80° C.

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* Oettel, *Zeit. f. Elektrotechnik u. Elektrochemie*, Band 1, 90.

12. ELECTROLYSIS OF A SOLUTION CONTAINING A FERROUS AND A FERRIC SALT.*

Prepare an iron sulphate solution in which half of the iron exists as ferrous oxide and the other half as ferric oxide. One liter should contain 10 grams of iron, together with 20 grams of sulphuric acid in excess. In three beakers, of equal capacity, introduce from 100 to 120 c.c of this solution. The kathode in beaker I is a platinum cylinder, while the anode is a spiral of platinum. In beaker II are similar electrodes with reversed polarity, while beaker III contains two strips of platinum of equal size. The three cells, together with the copper voltameter K, the amperemeter A, and the regulating resistance W (Fig. 15), are arranged in series, and a current varying from 0.3 to 0.4 ampere is sent through them.

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* Oettel, *Zeit. f. Elektrochemie*, Band 1, 90.

At the expiration of two hours the precipitated copper is weighed. The ferrous oxide still remaining in the three solutions is also titrated. It will be found that in beaker I the current exercised a reducing action in consequence of the low kathode current density. In II, because of low anode current density, oxidation took place; while in III, the two current actions about neutralized each other. The current efficiency, calculated by means of the copper voltameter, is invariably low, because, from the very nature of the solution, considerable losses must occur in the absence of a diaphragm. This is shown in the extreme case of III. The efficiency will be greater, and the difference between I and II be much more marked, if the solution for the experiment is very considerably diluted. Repeat the experiment, and substitute lead electrodes for the platinum electrodes. They should be the same size as the latter. It will be found that the oxidizing action is very much less than when platinum electrodes are employed.

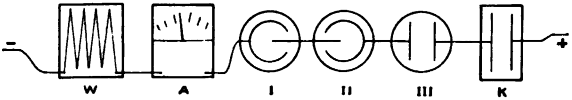

FIG. 15.

The experiment should also be made with carbon anodes. The portions of the anodes to which the binding screws are attached should be saturated with paraffin, so that the solution does not rise in them by capillarity and thereby damage the binding screws. It will be discovered that carbon anodes, in their oxidizing action, approach platinum very closely.

The oxidizing power of the various anode materials, with reference to ferrous sulphate solutions, is of extreme importance in the Siemens copper-recovery process (D. R. P., 42,243 and 48,959. Compare Experiment 21).

IV. Application of Gas Analysis to the Study of Electrochemical Reactions.

13. FORMATION OF HYPOCHLORITES AND CHLORATES.

The activity of a current in electrolysis is usually ascertained, at the conclusion of the experiment, by a qualitative and quantitative determination of the products of the reaction. It is true that in this way an average result only is obtained. It does not disclose whether, in the individual experiment periods, the yield has continued uniform, or whether it has varied, nor does it tell how much of the substance formed at one electrode has been destroyed at the other.

Should, however, gases be developed in the electrolysis, it is possible, as shown by the writer,* to examine these gases, and thus gain a deep insight into the changes which have played a prominent rôle. Indeed, it is possible to find out what has occurred at each of the two poles, and the reactions can be followed, minute by minute, through their entire course without the consumption of a drop of the liquid. No other method affords so rapid and so complete a supervision of the existing conditions. It is based upon the fact that an oxyhydrogen voltameter is introduced simultaneously into the circuit, and a comparison is made of the gases which have been produced in equal units of time in the voltameter and in the experimental cell. If secondary reactions have not occurred, these gases must be equivalent. If, for example, there have been developed in the voltameter 60 c.c. of electrolytic gas = 40 c.c. H + 20 c.c. O, there must have been formed in the decomposition of hydrochloric acid in a like period of time 40 c.c. H + 40 c.c Cl, and in the decomposition of ammonia, 40 c.c. H + 13.3 c.c. N. Should hydrogen be deficient, then work of a reducing nature has been done in the solution. If oxygen is wanting, or its equivalent of chlorine, etc., then something in the liquid has been oxidized. The portion of the total current consumed in reduction or oxidation is easily found from the ratio of the deficit to the theoretical amount (calculated from the electrolytic gas). An example, well adapted to prove all that has been said, and one that at the same time is very instructive, is the electrolysis of a potassium chloride solution without the use of a diaphragm. Several changes occur simultaneously. The gases appearing at first are hydrogen and chlorine. The latter is absorbed and reacts, with the caustic produced at the same time, to form potassium chlorate. At the commencement of the experiment some chlorine escapes. This fraction represents a current loss, which should be labeled "loss." As the process continues, a deficit of hydrogen is observed; this is due to the reduction of hypochlorite to chloride. This loss in current may be designated "reduction." Furthermore, oxygen will be found at the anode; it arises from the electrolytic decomposition of hypochlorite and chlorate. As electrolytic gas appears in this secondary electrolysis, this fraction of the current, also lost, may be designated "water decomposition."

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* Oettel, *Zeit. f. Elektrochemie*, 1894, 354.

In the entire calculation it is possible to start with hydrogen, as the following examples show:

I. Sixty c.c. electrolytic gas $=40$ c.c. H $+$ 20 c.c. O were obtained in the voltameter. The experimental cell at the same time gave 32 c.c. of gas $=30$ c.c. H $+$ 1.6 c.c. O $+$ 0.4 c.c. Cl. Deduct from the 30 c.c. H the quantities corresponding to the O and the unconsumed chlorine: $30-(3.2+0.4)=26.4$ c.c.

This quantity of hydrogen corresponds to the actual current yield. It equals, therefore:

	Per Cent.
$\frac{26.4}{40}$	66.00
The hydrogen deficit is 40—30 = 10 c.c. Consequently, the fraction of current used in the undesired reduction of hypochlorites is $\frac{10}{40}$	25.00
Water decomposition was effected by $\frac{3.2}{40}$	8.00
In the form of H—Cl gas, there was lost $\frac{0.4}{40}$	1.00
Total,	100.00

II. The voltameter showed 42.4 c.c. of electrolytic gas; the experiment gave 17.6 c.c. H + 0.4 c.c. O and no Cl.

		Per Cent.
Current yield (efficiency),	$\frac{17.6-0.8}{28.27}$	59.36
Water decomposition,	$\frac{0.8}{28.27}$	2.83
Reduction,	$\frac{28.27-17.6}{28.27}$	37.81

How much of the current efficiency is to be credited to the formation of hypochlorite and how much to chlorate, can, of course, be determined only by titration.

In performing experiments similar to those outlined, use a cylindrical vessel of about 150 c.c. capacity. It should be provided with a rubber stopper carrying the two electrodes and two narrow glass tubes. One of the glass tubes ends sharply under the stopper. It serves to conduct away the gases. The other tube extends to the bottom of the vessel, and is generally closed with a rubber cap. It is used to fill and empty the apparatus without taking the latter apart. The rubber stopper within the vessel hardens slowly, and closes the vessel very poorly if removed too frequently. The electrodes are two platinum wires, 1 mm. in thickness and from 20 to 25 cm. in length. They have a spiral form. When powerful currents are used, two small platinum plates with welded wires are preferable. A narrow glass tube is attached to the delivery tube by a short piece of rubber; it leads the liberated gases under a bell-jar, arranged as already described on page 18. An alkaline oxyhydrogen voltameter is also introduced into the circuit. The gases from it are also collected in a bell-jar. When practicable, the two bell-jars should stand in the same trough. The two movable glass delivery tubes should be so coupled with a piece of wire, that their ends can, with a jerk, be simultaneously brought under the two bell-jars, and by the same method be simultaneously removed. Collect 20 to 50 c.c. of gas in the experimental cell, and then turn the glass delivery tube to one side, without interrupting the experiment. Next, introduce the electrolytic gas, by means of a capillary tube, into the measuring burette. Read its volume after two minutes and then let it escape. In the same way measure the gas from the experimental cell. Absorb the chlorine in it with caustic potash and then the oxygen, by passing it into the phosphorus pipette. The residue is hydrogen. Every quarter- or half-hour test the activity of the current by gas analysis, and at the conclusion of the experiment determine the hypochlorite and chlorate by titration.

The experiment is made with (*a*) a 20 per cent. neutral potassium chloride solution, and current density of 200 to 1000 amperes per square meter, or (*b*) with a solution of 20 per cent. KCl + 2 per cent. KOH. The current conditions are the same as in the first instance. Variations in these conditions are secured by the choice of electrodes of unequal size, and by working at elevated temperatures. (Compare *Zeit. für Elektrotechnik u. Elektrochemie*, 1894, 356 and 474.)

N. B.—If, in gasometric investigations similar to those described, the analyst deals with explosive gas mixtures,—recognized by the fact that the gases from the voltameter and experimental cells are approximately equal in volume,—it is better to absorb the oxygen with pyrogallate of potassium instead of phosphorus. However, the danger of an explosion may be avoided by the addition of a measured volume of nitrogen.

14. ELECTROLYSIS OF HYDROCHLORIC ACID WITHOUT A DIAPHRAGM.*

A mixture of hydrogen and chlorine gas is obtained in the decomposition of hydrochloric acid, without a diaphragm. A very considerable loss of current occurs, due to the fact that the dissolved chlorine is reconverted at the kathode into hydrochloric acid. This loss, as indicated on page 45, diminishes as the density at the kathode increases. It may also be lessened in another way—viz., by the use of hydrochloric acid saturated with salts. Sodium sulphate is especially well adapted for this purpose, and a suitable solution may be made up as follows: 160 NaCl, 140 H_2SO_4, 700 H_2O. An ordinary short glass cylinder, or a flask from which the neck has been removed, will serve for the receptacle, the mouth of which is closed with a rubber stopper. Through the latter pass the two electrodes (strips of platinum with welded wire), a tube for the delivery of gases, and a second tube extending to the bottom of the receptacle, through which small quantities of liquid can be removed from time to time for testing purposes. As the chlorine and hydrogen liberated in this way recombine, at least partially, to hydrochloric acid under the influence of light, and in direct sun-light may give rise to explosions, it is advisable to work by gas-light.

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* Oettel, *Zeit. f. Elektrochemie*, Band II, 57.

The current yield is determined by absorption of the chlorine and subsequent titration, or by the gasometric method (Experiment 13) with the introduction of an oxyhydrogen voltameter.

The following points should be observed: Even with current densities of 500 amperes per square meter, the current efficiency will exceed 90 per cent. It begins to fall only when most of the free acid has been decomposed. With constant current strength the pressure gradually rises. Take out small portions of the solution from time to time, and ascertain the relation between the pressure and the remaining acid content. When an excess of sulphuric acid has been used, it will be observed, as the end of the experiment approaches, that a considerable and an increasing volume of oxygen escapes with the chlorine, and that eventually the liquid becomes almost free from chlorine. Should there be an excess of sodium chloride, however, gas evolution at the anode will finally cease, because the liquid has become neutral. Sodium hypochlorite will then be produced, and the reaction of the liquid, applied to a copper sulphate solution, will be alkaline. This experiment demonstrates the fact that by a little manual dexterity it is often possible to dispense with a diaphragm.

V. Experiments with a Diaphragm.

15. ELECTROLYSIS OF DILUTE SULPHURIC ACID (OR SODIUM HYDRATE) WITH A DIAPHRAGM: ION TRANSFERENCE.

In experiments made without a diaphragm, variations in concentration, due to the transference of the ions, are usually not perceptible. This phenomenon is, however, very noticeable as soon as a diaphragm is introduced. Concentration takes place either in the anode or kathode chamber, according to the nature of the process. In all electrolytic processes where a diaphragm is involved, attention should be directed to this point. The nature of the diaphragm exercises an influence, inasmuch as diffusion processes proceed concurrently.

Two battery jars with porous cups are filled with dilute sulphuric acid (1 : 20). The electrodes are cylinders of lead. The two cells are arranged in series, so that the external cylinder in one battery jar is the anode, and in the other the cylinder in the porous cup serves as such. The acid content is determined before the experiment is begun. A current of two or three amperes is then allowed to circulate for two hours, when the acid in the two chambers of each combination is again titrated. It will be discovered that in both cases the acid of the anode chamber is the more concentrated. This is due to the transference of the anion SO_4 to it. It is immaterial, therefore, whether the current density be high, as in one of these cells, or low, as in the other.

The experiment may be repeated with a similar arrangement of apparatus, using, however, a five per cent. sodium hydrate solution and electrodes of nickel or iron. In this case concentration will be observed in the kathode chamber, whither the sodium ions have passed.

16. ELECTROLYSIS OF A SALT SOLUTION WITH USE OF A DIAPHRAGM.

A cylindrical cup of sheet-iron, about 15 cm. wide and 12 cm. high, will answer both for receptacle and kathode (Fig. 16). In it there is a porous cup, the upper portion of which is either glazed or saturated with paraffin. It is closed with a rubber stopper, or with a wooden cover well paraffined and fixed by means of cement. Through the stopper passes a platinum wire with attached platinum plate. This is the anode. A gas delivery tube also fits into the stopper. A 20 per cent. salt solution, freed from lime and magnesia by means of soda, is filled into both inner and outer vessels. The exterior vessel is calibrated in the upper portion, so that during the experiment it will be possible to make determinations of the yield at definite intervals.

To this end the porous cup, filled and moistened throughout, is placed in the empty cylinder, and the liquid introduced into the latter until it is three-fourths full, when added volumes of 50 c.c. are successively introduced and marked on the porous cup with a lead pencil. A current of from three to five amperes is now sent through the liquid. Every hour an analysis is made of the escaping chlorine gas and of the kathode liquid.

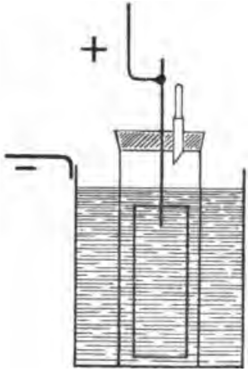

FIG. 16.

Sufficiently accurate results may be obtained if the burette is filled with a sodium chloride solution and the gas (about 50 c.c.) is rapidly read, then introduced into a bulb pipette, containing caustic potash for the absorption of the chlorine, and finally transferred to a phosphorus pipette to absorb the oxygen. A small gas residuum is nitrogen. In the calculation, this residuum, together with one-fourth its volume of oxygen, is recorded as air. Ten c.c. of the kathode liquid should be removed, and the alkalinity of the solution be determined by means of sulphuric acid and an indicator. The neutralized portion is diluted to 200 c.c., and 20 c.c. (= 1 c.c. of the original liquid) is then titrated with silver nitrate. The quantity of the titrating liquid (H_2SO_4 + $AgNO_3$) for each successive cubic centimeter of liquid taken, becomes constantly greater in consequence of the transference of the sodium to the outer solution. The quantity of NaOH produced may be calculated from the observed alkalinity and the volume of the kathode liquid. The current yield of NaOH diminishes with the rising alkalinity of the liquid, and the liberated chlorine becomes, at the same time, proportionately rich in oxygen. The changes in the yield are determined separately for each successive hour.

If the current strength be held constant, by frequent regulation, during the period of the trial, the necessary consumption of current, serving as a basis for the determination of the yield, may be directly calculated from the time; otherwise a copper voltameter should be introduced into the circuit, and the kathode be weighed every hour. An Aron ampere-hour meter may be substituted for the voltameter.

When carbon is used as the anode it is gradually attacked in consequence of the evolution of oxygen.

The oxygen is consumed almost quantitatively in the formation of carbon dioxide and humus substances, which impart a brown color to the anode liquid. Hence, if carbon anodes be used, the process can not be followed by gas analysis. Sodium hypochlorite and sodium chlorate will be formed in the anode chamber, but their quantity will be dependent upon the alkalinity of the liquid produced at the kathode, upon the temperature, and upon the porosity of the porous cup which has been used.

Note the pressure with every variation in current density, determine directly the decomposition pressure Z, and calculate from this, from the fall of potential V in the bath, and from the current strength *i*, the resistance *w* of the bath, by the formula:

$$V = Z + i.w$$

Also calculate, from the results of the experiment the production of NaOH from end-liquids, with varying alkalinity, per horse-power hour.

17. ELECTROLYSIS OF HYDROCHLORIC ACID WITH A DIAPHRAGM.

In the electrolysis of hydrochloric acid two points must be established: First, the high current yield of chlorine, approximating the theoretical very closely; second, the degree of purity of the liberated chlorine, which begins to contain oxygen after the hydrochloric acid in the anode chamber has been worked down to a great degree of dilution.

(*a*) *Determination of the Current Yield* (*Efficiency*).—A porous cup, paraffined in its upper portion, is placed in a small battery jar. The cup is closed with a stopper of gypsum or wood, provided with openings for the carbon anode, and for two glass tubes. The stopper or cover, as well as the upper portion of the carbon anode, is saturated with paraffin. A cylinder of sheet-copper, with its attached wire, and encircling the porous cup at some distance, constitutes the kathode. The electrolyte is a ten per cent. solution of hydrochloric acid. A copper voltameter inserted in the circuit serves as a meter. When the cover of the porous cup has been well secured with cement, the experiment may be begun. A current of about two amperes is sent through the apparatus for several hours, and an air-current is simultaneously drawn through the porous cup by means of an air-pump. The purpose of this is to draw the liberated chlorine through two absorption flasks filled with dilute caustic soda. While the current is interrupted, for the purpose of weighing the copper, the air-current is continued in order to collect the greater portion of the chlorine dissolved in the hydrochloric acid. The contents of the two absorption vessels are then united; a definite volume of the liquid is boiled with an excess of ferrous sulphate solution and sulphuric acid (for the determination of the chlorine), and finally titrated back with potassium permanganate. The direct iodometric determination of the chlorine by means of acetic acid and potassium iodide, with subsequent titration by means of thiosulphate, is liable to prove faulty, because, in addition to the hypochlorite of sodium, chlorate of sodium also may have been produced. The hydrochloric acid containing chlorine, which is in the porous cell, is also diluted to a definite volume, and the free chlorine present in it is thus determined. The ratio between the chlorine found by the two titrations and that calculated from the precipitated copper represents the current yield (efficiency).

The analyst should satisfy himself that the carbon has not been attacked. For comparison, conduct an experiment with dilute sulphuric acid, and observe that in this case the carbon is very rapidly destroyed by the liberated oxygen.

(*b*) *Testing the Purity of the Chlorine.*—Inasmuch as difficulties are encountered in the gasometric study of the chlorine when the porous cup is completely closed by a cover, it is better to use a rubber stopper and an anode of platinum, because with a carbon anode the oxygen will be entirely, or at least in part, consumed in oxidations, and its determination will be accompanied with error. The experiment should be conducted with a current of from two to four amperes. The liberated chlorine should be drawn at intervals into a gas burette, and carefully examined in the manner already indicated in Experiment 16.

18. FORMATION OF PERSULPHURIC ACID BY THE ELECTROLYSIS OF SULPHURIC ACID.*

The formation of persulphuric acid, $H_2S_2O_8$, constitutes an interesting example of the fact that the ions separated in an electrolysis can recombine to form a new compound, the two anions (HSO_4) uniting to form one molecule of persulphuric acid, $H_2S_2O_8$. Usually some hydrogen peroxide results from secondary reactions. The concentration of the sulphuric acid used, the temperature, and the current density at the anode exercise an important influence on this reaction.

The following apparatus has been found practicable for the execution of this experiment. A small porous cup of 100 c.c. capacity is placed in a beaker glass of such a size that the circular space without the porous cup will contain 100 c.c. The kathode is introduced into the porous cup; it consists either of a plate of platinum or of lead. It should be the same in all experiments. For anodes use (*a*) a platinum plate of 20 sq. cm. with attached platinum wire, (*b*) a platinum wire of two sq. cm. active surface. This latter may be constructed in the following way:

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* Compare O. Schönherr, "Studien über die Bildung von Ueberschwefelsäure," Inaugural-Dissertation, Giessen, 1895; also *Zeit. f. Elektrochemie*, Band I, 417, 468; Band II, 245.

A platinum wire (p) (Fig. 17), 0.5 mm. in thickness and 17 cm. in length, is soldered at one end to a heavy copper wire (k); 127 mm. from the other end is placed a button of fusible glass. The glass tube (g) is pushed over the copper wire until it reaches the drop of fusible glass, with which it is then united. The projecting platinum wire, having exactly two

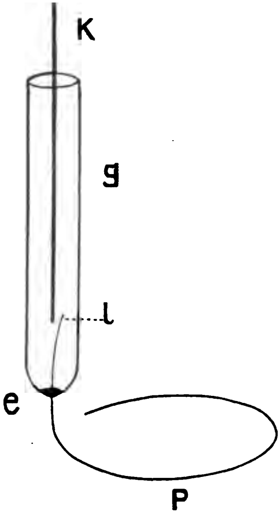

FIG. 17.

sq. cm. surface, is bent at right angles to a ring which in the experiments encircles the porous cup horizontally in the middle of the liquid layer.

I. *Influence of Concentration.*—One hundred c.c. of cold sulphuric acid, specific gravity 1.15, is introduced into the beaker glass. The porous cup, moistened with the same acid, is also introduced, and filled with the acid until the liquid within and without the cup stands at the same height. The beaker glass is placed in a vessel with flowing water, or, what is better, in ice-water. A thermometer is suspended in the acid of the beaker glass, and the temperature noted from time to time. The anode is the platinum wire above described. It is held in position by an electrolytic stand. A current of two amperes is allowed to act for one hour. At the expiration of half an hour, and also at the conclusion of the experiment, two samples (five c.c. each) of the anode acid are removed for the determination of the persulphuric acid and the hydrogen peroxide. (Experiment I(*a*).)

Proceed in precisely the same way when using sulphuric acid of 1.3 and 1.45 specific gravity. (Experiments I(*b*) and I(*c*).)

II. *Influence of Current Density.*—Electrolyze 100 c.c. of sulphuric acid, specific gravity 1.3, for one hour with two amperes:

(*a*) Using a plate of platinum with 20 sq. cm. surface (anode current density — $D_a = 1000$ amperes per square meter); (*b*) using a platinum wire of two sq.

cm. surface ($D_a = 10{,}000$ amperes). By further reducing the anode surface—*e.g.*, to 0.4 sq. cm.—it is impossible, even with increasing pressure, to electrolyze more concentrated acid in the cold. Upon the gradual application of heat, the passage of the current begins, and at a certain point there suddenly occurs a tumultuous decomposition. The experiment may be readily conducted in a small glass dish without the use of a diaphragm.

III. *Influence of Temperature.*—One hundred c.c. of sulphuric acid, specific gravity 1.3, are electrolyzed with two amperes and a wire anode for a period of one hour. The beaker glass is placed—

(*a*) In a freezing mixture of ice and salt.

(*b*) In water having the temperature of the room.

(*c*) In water ranging from 60° C. to 70° C.

IV. *Analysis.*—The analytical investigation is based upon the following reactions:

1. $H_2S_2O_8 + 2FeSO_4 = Fe_2(SO_4)_3 + H_2SO_4$.
2. $H_2O_2 + 2FeSO_4 + H_2SO_4 = Fe_2(SO_4)_3 + 2H_2O$.
3. $5H_2O_2 + 2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$.
4. $10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$.

If the customary solution of 3.16 grams of $KMnO_4$ in a liter has been used, then every cubic centimeter of it will correspond to 0.0097 gram $H_2S_2O_8$ and to 0.0019 gram H_2O_2. The sample under examination (5 to 20 c.c., according to its content) is diluted to from 200 to

300 c.c., with water. An excess of ferrous ammonium sulphate is added, and the solution is then stirred, after which it is *allowed to stand quietly for from five to ten minutes*, when the excess of iron is titrated back with permanganate. The iron used, or its equivalent of permanganate, represents the sum $H_2S_2O_8 + H_2O_2$. To obtain trustworthy results, it is absolutely necessary to allow the solution to stand quietly for some time, because persulphuric acid acts slowly upon an iron salt in dilute solution. This is especially true when the iron salt is present in very slight excess.

The hydrogen peroxide formed may be determined in a separate sample by direct titration with permanganate according to equation 3. The difference in the numbers obtained in the two titrations corresponds to the quantity of persulphuric acid which has been formed.

VI. Metal-precipitations with Soluble and Insoluble Anodes.

19. COPPER REFINING.

A typical example of work done with soluble anodes, as well as the precipitation of a metal from aqueous solution, is shown in the electrolytic copper-refining process. The chief conditions for metal refining are: First, thorough agitation of the electrolyte, in order that a sufficient quantity of metal for precipitation may be at all times present in the vicinity of the kathode. Second, the selection of a proper current density to obtain the precipitate in the desired form. The higher the current density, the richer should the liquid be, and the more thoroughly must it be agitated, if the precipitation of impurities is to be avoided. A portion of the impurities will continue attached to the anode as a porous mass—"anode mud." This gradually falls to the bottom of the vessel, while another portion of the impurity dissolves and slowly vitiates the bath. The agitation of the liquid must not be so energetic as to detach the "anode mud" or stir it up, otherwise it will be mechanically admixed with the pure precipitate. The chemical composition of the electrolyte is employed to assist the activity of the current. Thus, sulphate liquors are chosen, if the solution is to be protected from lead, and in the case of copper they should be acid to prevent the simultaneous precipitation of iron and nickel.

Experiments upon the deposition of metals from aqueous solution should not be conducted upon too small a scale. A kathode surface of at least one sq. dm. should be used, otherwise the metal precipitation will not be uniform, and at its edges will show an entirely different character from that deposited in the middle of the surface.

The most suitable vessels for this purpose are glass troughs. In cases of necessity, battery jars or paraffined cigar-boxes may be used. The solution can be agitated by means of a stirrer, or by conducting a current of hydrogen through it, care being taken not to disturb the "anode mud."

To show the influence of agitation in liquids, suspend two plates of copper in an acidulated copper solution contained in a beaker glass. Allow a current of about 0.5 ampere to act through the night, and do not disturb the liquid.

In ordinary experiments it is customary to use a solution of 150 copper sulphate + 50 sulphuric acid in 1000 of water. The anodes are two thick copper sheets extending almost to the bottom of the trough. The metal composing these sheets should be as impure as possible. Another sheet of copper, suspended between the anodes, is the kathode. Its distance from each anode is about 30 mm. The liquid is agitated and the work is continued for at least twenty-four hours with current densities ranging from 50 to 200 amperes per square meter. Note the pressures, as well as the character of the precipitate, and make a determination of the yield. When the anode material is not sufficiently impure, certain adulterants—*e.g.*, Fe, Ni, As, and Sb—may be purposely introduced into the liquor. Then observe how much of these individual substances must be added, with the prevailing current density and circulation, before the precipitate becomes impure. The deportment of arsenic is especially instructive and striking.

Examine the "anode mud" for the noble metals which have accumulated in it, and attempt to regenerate again, in a simple manner, liquors which have become useless. At the conclusion of these observations project a plan for the daily production of 500 kilograms of electrolytic copper: what size of baths is needed, judging from the observed favorable current density? How many baths are required? What should be the dimensions of the dynamo? How much horse-power is required? How much liquor must be used in the baths? When the composition of the anodes is given, what time must expire before the liquors become useless, and how much copper will have been worked up in the plant during that period?

20. COPPER PRECIPITATION WITH INSOLUBLE ANODES.*

In sulphate liquors it is frequently possible to use sheet-lead as the anode. As the oxygen is evolved, the lead becomes coated with a layer of dioxide, which slowly separates in leaf-like forms. It is, of course, understood that the liquor must not contain either chlorine or nitric acid. In the present example this deportment is to be observed and a simultaneous study is to be made showing the dependence of the electrolytic separation of two metals upon the current density. Other conditions being the same, a current density will be found for every possible mixture below which a satisfactory separation can be obtained, but if this density be exceeded, the metals will be precipitated together.

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* Oettel, "Anleitung zu elektrochem. Versuchen," p. 109.

One hundred and fifty grams of copper sulphate are dissolved in a liter of water with the addition of fifty grams of sulphuric acid. The solution is digested with an excess of finely-divided arsenic, filtered when cold, and electrolyzed in a glass trough with two lead anodes, between which there is suspended a plate of copper serving as kathode (surface one or two sq. dm.; electrode separation about 20 mm.). The solution is thoroughly mixed by an agitator or by an air-current. At the beginning use a current density of 150 amperes per square meter. Note the pressure and the moment when the red copper precipitate commences to take on a gray color due to co-precipitated arsenic. At this point determine the copper and arsenic content of the liquid. Continue the experiment with a new copper plate equal in size to that used before. Lower current density (about 100 amperes) should be employed. Lower bath-pressure will now prevail, and for a time the copper will precipitate in satisfactory form, but finally it will show a deposit of arsenic. Again determine the copper content of the liquid (the arsenic content will not have changed), and continue the experiment a third and a fourth time, always with lower current densities. Finally, arrange the results in a table showing to what degree the liquor can be deprived of copper by the separate current densities, without co-precipitating arsenic, and what pressure should prevail in the bath.

It is instructive, with the experience that has been gained, to carry out the electrolysis of a large quantity of liquor, probably a liter, without interrupting the process, in such a manner that copper is obtained actually free from arsenic. To this end arrange a series of test-tubes, with varying copper content, for a colorimetric determination of the experimental liquor, reducing the current strength each time when the colorimetric test shows that, according to the numbers of the table, the danger-point has been almost reached. The resulting electrolytic copper is examined in the following manner for small quantities of arsenic: Five grams of copper are dissolved in ten c.c. of nitric acid, specific gravity 1.2. The nitrous acid is boiled off, the liquid is diluted to 50 c.c., and ten grams of ammonium nitrate and a little potassium bichromate are added, after which the solution is brought to boiling and ten c.c. of a slightly alkaline solution of ammonium molybdate are introduced. Filter out the yellow precipitate obtained after boiling five minutes, wash it with a ten per cent. solution of ammonium nitrate, then dissolve it in dilute ammonia, and, after filtering, introduce some magnesia mixture. The volume of liquid should equal from 20 to 30 c.c. If, after one hour, despite the rubbing of the walls with a glass rod, a white crystalline precipitate of magnesium ammonium arsenate has not separated, then the arsenic content of the precipitated copper is less than 0.01 per cent. If the precipitate should not have its characteristic appearance, examine it under a microscope. It must consist of fine needles which are often united to stellate masses.

VII. Introduction of Aid-reactions.

21. EXPERIMENT WITH SIEMENS' COPPER PROCESS.

This process is based on the use of a solution containing $2FeSO_4 + CuSO_4$, together with excess of sulphuric acid, which is conducted through a bath provided with a diaphragm. The liquor is first conveyed to the kathode, where it is deprived of as much copper as possible, and then led to the anode, and there the anion SO_4, which has separated from the copper sulphate, unites with the ferrous sulphate to form ferric sulphate. The latter is again brought in contact with Cu or Cu_2S outside of the bath; the Cu is dissolved with re-formation of $FeSO_4$ and $CuSO_4$. (See Oettel, "Anleitung zu elektrochem. Versuchen," p. 77.)

In performing the experiment, use a battery jar with a tubulure at its bottom. A porous cup is placed in the jar. A cylinder of copper, standing in the porous cup, serves as kathode, while without, in the battery jar, are several carbon plates used as anodes. The carbon plates are paraffined at the points where they come in contact with the binding screws. The solution, consisting of 200 grams of ferrous sulphate + 80 grams of copper sulphate + 60 grams of sulphuric acid in 1000 of water, is continuously introduced at the bottom of the porous cup by means of a funnel tube. The liquid overflows into the battery jar, where it is held in equilibrium by means of the tubulure and a movable tube for adjusting the level. The added liquid is blue in color, while that which flows away should be green and is regenerated by filtering it through cementation copper. The composition of the liquid is accurately determined, during the period of experimentation, by titration with potassium permanganate.

These points should be observed :

1. The pressure in the bath with varying current densities.

2. The rise in pressure of the bath, and the fall of current strength with insufficient circulation of the liquor.

3. The current efficiency in metallic copper. During this determination a copper voltameter is inserted as a current meter.

4. Regulate the inflow of liquid so that the outflowing liquor contains as much ferric sulphate as

possible, and consequently as little copper as possible.

5. Let the operator satisfy himself that by using lead anodes, instead of anodes of carbon, the action will proceed in such a manner that the liberation of oxygen will occur without material formation of ferric salts. At the same time, the current strength being unchanged, the pressure will be much higher, because the aid-reaction, tending to diminish the pressure, is absent.

6. Determine the pressure of decomposition by using (*a*) carbon anodes and (*b*) lead anodes. This is done by interrupting the current after a long experimental period and rapidly inserting in the circuit a voltmeter with high resistance and good damping. This insertion is best made by means of a commutator. Weston voltmeters, or galvanometers with high series resistance, and copper or oil damping, are especially well adapted for this purpose.

7. If the experiment be conducted in a beaker glass *without* the use of a diaphragm, it will be noticed that at the kathode the liquid which has become poor in copper and consequently specifically lighter, will rise, whereas at the anode the liquid will flow down in heavy layers and form a green-colored zone at the bottom. The analyst should attempt to build up a method of work, dispensing entirely with the use of a diaphragm.*

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* Compare Coehn, *Zeit. für Elektrochemie*, Band II, 29.

An analogous experiment may be conducted with a hydrochloric acid solution of cuprous chloride in a solution of salt (Höpfner process). Half of the cuprous chloride in the kathode chamber will be reduced to metal, while the other half, in the anode chamber, will be oxidized to cupric chloride. It is well to note that in this instance the copper acts as a monad, and hence the quantity of it precipitated is twice as great as that thrown out of the sulphate solution.

VIII. Experiments with Molten Electrolytes.

22. PREPARATION OF MAGNESIUM.*

(*A*) *Crude Material.*—Fuse artificial carnallite, $KMgCl_36H_2O$, by frequent additions, in a graphite crucible at as low a temperature as possible. The salt melts at first in its water of crystallization. The latter escapes with foaming, and the mass again becomes quiet, and is perfectly molten. In the first phase of the reaction, the salt-cake must be frequently pushed down with a piece of wood to avoid an overflow. As soon as the fusion has acquired a dull-red heat, stir a little sawdust into it by means of an electric-light carbon. The purpose of this is to destroy any magnesium sulphate which may be present. The action is complete upon the breaking forth of flames of carbon monoxide.

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* Oettel, *Zeit. für Elektrochemie*, Band II, 394.

$$MgSO_4 + C = MgO + SO_2 + CO.$$

When a small portion of the fusion shows nothing more than traces of sulphuric acid, the operation is at an end. Discontinue stirring, in order that the separated magnesia may collect upon the bottom of the crucible, and carefully pour off the fused mass from the settlings into an iron mold. On cooling, it crumbles into pieces, and is immediately transferred to tight-fitting vessels.

(*B*) *Electrolysis.*—The author has already shown (*l. c.*) that satisfactory results can be obtained only by preventing the action of moist gases upon the fusion. The latter, furthermore, must be as free as possible from sulphates and magnesium oxychloride. A slight addition of fluorspar is beneficial. It dissolves the thin layer of magnesia, which frequently surrounds the metallic globules, and facilitates the union of the latter to larger metal masses. The arrangement of the experiment is shown in Fig. 18.

A rather large porcelain crucible is elongated by fastening above it, by means of a wire, a cylinder of asbestos paper. The purpose of the paper is to exclude the gas flame from the interior of the crucible. A diaphragm of asbestos paper is also placed in the middle of the crucible. The lower portion of this diaphragm is perforated like a sieve. Above, where it comes in contact with the surface of the fusion, it is intact. This arrangement prevents the chlorine, separating at the surface of the anode chamber and there producing a thin foam, from penetrating into the kathode compartment. The kathode consists of a strip of bright sheet-iron, about ten mm. in width, while the anode is a piece of cored carbon from the cavity in which, for several centimeters, the graphite filling is removed for the reception of the copper conducting-wire. The experiment is made with a current of three to ten amperes at a dull-red heat, a little above the fusing-point of magnesium. The diaphragm

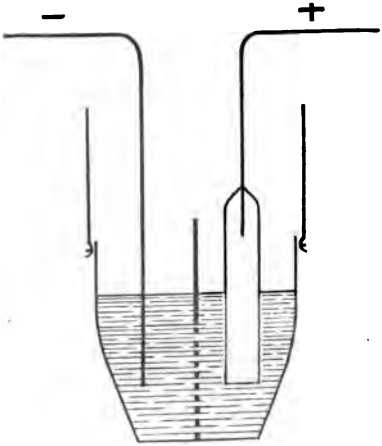


FIG. 18.

is removed when the experiment is ended. A little fluorspar is thrown into the crucible at this point, and the contents stirred with the metal strip serving as kathode. All the liberated magnesium will be united in larger globules. So long as the temperature of the fusion does not exceed a moderate red heat, the contents of the crucible may be poured without hesitancy into a mold, there being no danger that the magnesium will inflame. Calculate, from the bath-pressure and the current efficiency, the consumption of power for the daily production of 20 kilograms of magnesium.

23. ELECTROLYSIS OF FUSED LEAD CHLORIDE.

Use the apparatus just described in the experiment for the production of magnesium. It is not necessary that the diaphragm should extend to the bottom; it will suffice if it dips one cm. into the fused mass, so as to prevent the chlorine foam from spreading to the kathode. The lead drops to the bottom of the crucible and there collects in a globule. At the conclusion of the experiment pour the crucible contents into a conical mold. When the mass has solidified, the lead can easily be separated and weighed.

Observe the pressures corresponding to the various current densities, determine the current efficiency, and calculate the power, as well as the number of baths, necessary for the daily production of 1000 Kg. of lead, assuming that 500 amperes are to be conducted into each bath.

(An instructive example in the electrolysis of a molten mass is given by Lorenz, *Zeit. für Elektrochemie*, Band II, 318.)

24. ELECTROLYTIC PRODUCTION OF ALLOYS.

If, when preparing light metals electrolytically, there be introduced upon the bottom of the vessel containing the electrolyte a molten layer of some heavy metal, and this be connected during the electrolysis with the negative pole of the battery, alloys will be directly formed. Aluminium bronze was formerly prepared at Neuhausen by placing a layer of copper, serving as kathode, under molten clay, while a carbon anode dipped into the mass. At the present time the same principle is used in making lead-sodium; fused lead is the kathode, and fused caustic soda or salt is the electrolyte.

The preparation of an alloy of tin and magnesium constitutes a good laboratory experiment. Fuse carnallite, with the addition of some fluorspar, in a porcelain crucible having an asbestos elongation. Introduce ten grams of tin into the crucible, and let a stout iron wire dip into it. The iron wire is surrounded by a glass tube in such a manner that but five mm. of the wire project into the tin. This affords a good contact with the molten mass, and the wire is sufficiently isolated in other respects. The anode is a piece of carbon. All that has been said in regard to carnallite on page 72 applies in this instance. A diaphragm is unnecessary.

When the carnallite contains sulphate, the resulting alloy will contain sulphur, and generally silicon, reduced from the crucible wall, which consequently becomes brown in color. Analyze the resulting brittle alloy.

IX. Experiments with Multipolar Electrodes.

25. PRECIPITATION OF COPPER BY MEANS OF DOUBLE-POLE ELECTRODES.

If, during the passage of a current between two electrodes, there be suspended between the latter an isolated strip of metal, this also becomes an electrode. Indeed, it is a double-pole electrode, for the side turned toward the kathode acts as an anode, and that toward the anode acts as kathode. Consequently, the combination conducts itself like two cells in series. The phenomenon is not limited to the use of a single intermediate plate. Many such can be introduced when the pressure at the end electrodes is sufficiently high. If the electrodes completely fill the cross-section of the trough, the entire current passes through the intermediate plates. Should they, however, only partially fill out the cross-section, then very considerable portions of the current will escape the middle plates and pass directly through the liquid. Having *n* intermediate plates, consequently $n + 2$ electrodes, the combination will act like $n + 1$ cells in series. If, at the same time, the current strength i prevails, the total electrochemical action corresponds only to $(n + 1)i$, even when the intermediate plates separate the trough into $n + 1$ perfectly water-tight chambers. If the intermediate plates are only suspended in the solution, the total action is less. The advantage of the arrangement consists in the small number of contacts per cell. It is already variously applied on the large scale. The author has proposed to call this new arrangement "chamber arrangement." The relations are most simply shown by using copper electrodes (Fig. 19). Suspend in a rectangular glass vessel of at least from five to ten cm. cross-section a number of copper plates, filling out the cross-section almost completely, and removed from each other by two cm. The filling liquid is a copper sulphate solution with an excess of sulphuric acid. The arrangement of the

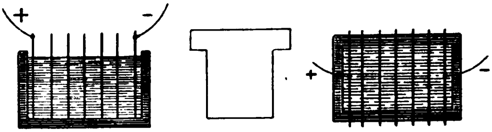


FIG. 19.

vessel shows similarity to a copper voltameter. The current strength is so controlled that there is a current density of one ampere for each square decimeter. Care should be taken to have the electrolyte thoroughly mixed. The separate electrodes should be numbered and weighed.

Note the following: First, the middle electrodes have double poles; that is, copper will be precipitated as a bright crystalline coating on the one side, while it will dissolve from the other side, causing the latter to become rough and discolored. This side will also be coated with " anode mud."

Second, the total pressure of the bath is the sum of the individual pressures between the separate electrodes.

Third, the positive end plate constantly becomes lighter in weight, while the negative end plate grows correspondingly heavier. The weight of the intermediate plates scarcely changes, because the solution and precipitation are approximately equal.

Fourth, if at the beginning the intermediate plate has been covered on the kathode side with an exceedingly thin layer of fat, or if it has been rubbed over with graphite, it will be possible, after the experiment has been continued for some time, to strip off the precipitated copper as a sheet, and in this way the quantities of copper deposited upon the separate intermediate plates may be directly weighed.

Fifth, the analyst should satisfy himself in accordance with the preceding paragraph that the quantity of copper deposited on the intermediate plates rapidly diminishes if these plates fill out the cross-section of the trough but partially.

Sixth, replace one of the intermediate plates by a sheet of lead. This will show clearly that the current strives to avoid the intermediate plate because the copper precipitate upon the one side of the lead sheet does not extend to the edge. Determine the pressure between the plate and the adjacent electrode. It will be discovered to be appreciably higher than that existing between the remaining electrodes, because the lead acts as an insoluble anode with oxygen liberation.

26. ELECTROLYSIS OF SALT SOLUTIONS WITH A MERCURY KATHODE.

The electrolysis of a salt solution with mercury, according to the suggestion of Castner, is at the present time the most important example of work with double-pole electrodes. Mercury serves at one point as a kathode, where it takes up sodium. It then circulates to the anode chamber and there serves as anode in that it gives up its absorbed sodium to produce caustic soda. It is very necessary that there should be a rapid circulation of the mercury, otherwise there will be too great an accumulation of sodium, which will crystallize out in the form of amalgam—a brittle mass.

The experiment is performed in a flat glass dish (Fig. 20), with an even bottom, upon which is poured a layer of mercury five to seven mm. in depth. A bell-jar carrying the platinum anode, A, and a gas delivery tube is so suspended that it dips securely into the mercury. The kathode is an iron spiral, K. A rotating iron wire, D, extending with its horizontally bent end under the mercury, produces the circulation of the latter by rotation of the entire mass. A saturated salt solution is poured into the bell-jar. Without, in the dish, is a measured quantity of dilute caustic soda of known content. This increases during the electrolysis. Conduct the experiment with three to five amperes. At first make a short circuit between the kathode and the mercury, in order that a definite quantity of sodium may accumulate in that metal. Interrupt the short circuit after a while, and continue the electrolysis for several hours.

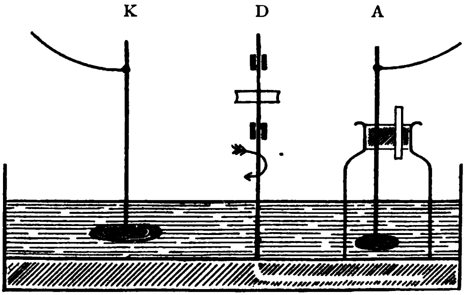


FIG. 20.

Determine the pressure between the end electrodes as well as that between the mercury and the end electrodes; also determine the current yield and the purity of the liberated chlorine. The operator should furthermore prepare sodium amalgam in some simple electrolytic way and determine its relative stability toward pure water. The amalgam completely surrenders its sodium to the water very slowly, but very rapidly when it comes in contact with dilute acid, or when, in the course of electrolysis, hydroxyl ions are separated at its surface.

X. Organic Electrolysis.

(*Prof. Dr. K. Elbs.*)

27. THE ELECTROLYSIS OF SODIUM ACETATE.

In concentrated solutions, at low temperatures and with high current density at the anode, the electrolysis of sodium acetate proceeds mainly in the direction of the following equations:

1. $CH_3\,COONa = \overset{+}{Na} + CH_3\,\overset{-}{COO}$.
2. At the kathode: $2Na + 2H_2O = 2NaOH + H_2$.
   At the anode: $2CH_3.COO = CH_3\,CH_3 + 2CO_2$.

The current efficiency in ethane equals more than 90 per cent., and that of carbon dioxide almost 100 per cent. of the theory. The ethane, after the absorption of the carbon dioxide, is contaminated only with traces of ethylene and oxygen.

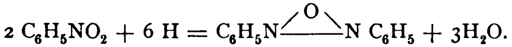
A cylinder of nickel gauze, placed in a beaker glass, serves as kathode. It surrounds a porous cup in which there is a small platinum spiral acting as anode. A loose-fitting glass tube is fastened into the upper fourth of the porous cup with gypsum. It is closed with a stopper, through which pass the anode conducting wire and a gas delivery tube. The gas first passes through a Geissler potash bulb, in order to absorb and weigh the carbonic acid, and is then collected over water. The anode and kathode liquids are almost saturated, cold, aqueous solutions of sodium acetate, acidulated with a few cubic centimeters of glacial acetic acid. The current density at the anode should be at least 100 to 120 amperes per sq. dm. The temperature of the bath should not exceed 20° C.; it should be cooled with ice-water. When the hydrogen and the ethane are to be collected together the operator can dispense with the porous cup. A wide-mouth glass vessel can be used. Through its stopper pass not only the conducting wires from the anode and kathode, but also a gas delivery tube. This vessel can be more easily cooled; and, moreover, its internal resistance will be less. Furthermore, it is possible, by suitable devices and without the use of a porous cup, to collect the gases from the anode and kathode separately in suitable vessels.

28. REDUCTION OF NITROBENZENE TO AZOBENZENE.

The reduction of nitrobenzene in alkaline solution proceeds according to the following equation:

$$2\,C_6H_5NO_2 + 8\,H = C_6H_5N = N\,C_6H_5 + 4\,H_2O.$$

The rearrangement, however, can not be carried out so that azobenzene alone will result, because, when the reduction has proceeded far enough to produce azoxybenzene, some hydrazobenzene will have been formed:



$$2\,C_6H_5NO_2 + 6\,H = C_6H_5N\overset{O}{\overline{\qquad}}N\,C_6H_5 + 3H_2O.$$

$$2\,C_6H_5NO_2 + 10\,H = C_6H_5NH - NH\,C_6H_5 + 4H_2O.$$

A solution of 25 grams of nitrobenzene in 350 c.c. of alcohol is mixed with sodium hydrate made from 40 grams of caustic soda and 50 grams of water. This mixture is poured into a tall beaker glass which is filled to one-third with the liquid. In this solution is placed a porous cup containing a 20 to 30 per cent. aqueous caustic soda solution as anode liquid. The porous cup must have been thoroughly moistened with sodium hydrate before its introduction into the nitrobenzene solution; otherwise its pores will be obstructed by the accumulated nitrobenzene. Instead of the porous cup, there may be substituted a bag of thick unbleached muslin, the threads of which have become swollen by lying several days in dilute caustic soda. Such muslin resists the action of alkaline liquids better than the ordinary porous cups. The kathode and anode are cylinders of nickel gauze. If the solutions are introduced while warm, and rather strong currents are used, the heat of the current will suffice for the production of the temperature most favorable to the reaction (boiling-point of alcohol). The upper portion of the beaker glass, not moistened by the liquid, acts during the experiment as a condenser, so that but very little alcohol escapes. The loss can, from time to time, be replaced. The current density at the kathode may vary from 1.5 to 2 amperes for one sq. dm. without the occurrence of a notable evolution of hydrogen. The active surface of the gauze may be assumed, with sufficient accuracy, as equal to that of a plate of metal of like size with double surface. When more than a calculated amount of current is conducted through the bath, the kathode liquid, which changes in color from yellow through orange to brown-red, again becomes clear and has a yellowish red color, at which point the current is interrupted. The solution now contains chiefly azobenzene, no nitrobenzene, very little azoxybenzene, and not much hydrazobenzene. It is poured, while yet hot, into an Erlenmeyer flask and exposed for some hours to the action of a slow current of air, which is drawn through it, and by means of which the hydrazobenzene is oxidized to azobenzene:

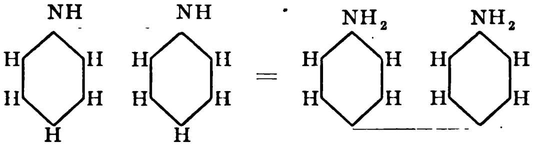
$$C_6H_5NH-NHC_6H_5+O=C_6H_5N=NC_6H_5+H_2O.$$

The greater portion of the azobenzene crystallizes out, and after filtration is almost chemically pure. Any residue may be precipitated out by the addition of water or driven out by steam. The substance will be pure after one re-crystallization from alcohol or from petroleum ether. The yield, calculated from the current used, will be 80 to 90 per cent. of the theoretical, while calculated upon the nitrobenzene it will be 90 per cent. of the theory.

29. PREPARATION OF HYDRAZOBENZENE AND BENZIDINE FROM NITROBENZENE.

Proceed as in the reduction of nitrobenzene to azobenzene. Do not, however, interrupt the current when the kathode liquid begins to acquire a light color, but continue the reduction for an hour longer; at the same time diminishing the current, in order, by lessening the current density to limit the useless evolution of hydrogen. The hot kathode liquid is poured into an Erlenmeyer flask, mixed with a few drops of ammonium sulphide, and the flask is then corked and placed to one side for crystallization. The mother liquor, from the first crystallization, is freed from a portion of its alcohol by distillation. On cooling, more of the hydrazobenzene crystallizes out, contaminated, it is true, with more or less azobenzene. The current efficiency is 60 to 70 per cent. and the yield calculated upon the nitrobenzene is the same.

To convert the hydrazobenzene into benzidine according to the equation



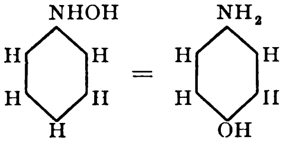
strongly acidify the kathode liquid with ordinary hydrochloric acid, boil, and precipitate the benzidine as sulphate by the addition of a saturated solution of Glauber's salt. Filter out the sulphate after standing several hours, then cover it first with water, afterward with alcohol, when it will be found to be almost pure. The yield exceeds 60 per cent. of that calculated from the nitrobenzene.

30. REDUCTION OF NITROBENZENE TO p-AMIDOPHENOL.

The conversion of nitrobenzene into p-amidophenol proceeds by two steps: Phenylhydroxylamine is first formed, and when this is treated with sulphuric acid it is re-arranged into the sulphate of p-amidophenol

1. $C_6H_5NO_2 + 4H = C_6H_5.NH.OH + H_2O$.

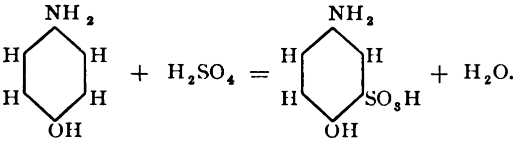
2.



It is best to use an anode and kathode of platinum. Ordinary concentrated sulphuric acid will do for the anode liquid, while the kathode liquid consists of a solution of 20 grams of nitrobenzene in 150 grams of pure concentrated sulphuric acid, to which have been added *a few drops* of water. The diaphragm is a porous cup, thoroughly moistened with sulphuric acid. The current density at the kathode may reach six amperes for one sq. dm. The reduction is accelerated by heating from 60° to 90° and occasionally stirring the kathode liquid. Twice the amount of current required by theory should be introduced. The deep blue contents of the porous cell are poured, while yet hot, into a beaker glass. They congeal on standing in a cool place to a crystalline mass of crude p-amidophenol sulphate. This should be filtered through asbestos with the aid of a suction pump, and dried on a porous plate. It may then be crystallized from hot dilute alcohol. Calculated upon the nitrobenzene the yield varies from 20 to 50 per cent. of the theoretical. The chief secondary products are dye-stuffs, aniline sulphate, and p-amidophenol-sulphonic acid. The aniline is formed by the complete reduction of the nitrobenzene:

$$C_6H_5NO_2 + 6\ H = C_6H_5NH_2 + 2\ H_2O,$$

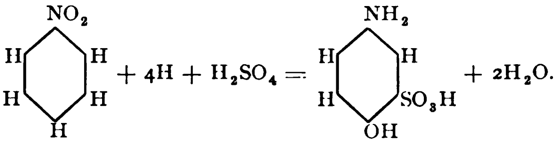
while the p-amidophenol-sulphonic acid is produced by the action of sulphuric acid upon the original p-amidophenol:



The aniline sulphate remains in the mother liquor. When the p-amidophenol sulphate is re-crystallized the sulphonic acid remains undissolved.

31. PREPARATION OF p-AMIDOPHENOL-SULPHONIC ACID FROM NITROBENZENE.

The reaction proceeds according to the equation

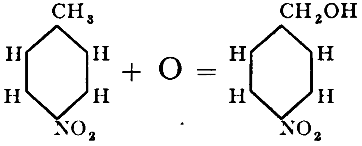


Use a beaker glass as bath with a large platinum kathode and a porous cup containing the platinum anode. The beaker glass is surrounded either with asbestos-paper or it is placed in a large vessel filled with finely divided sand. The anode liquid should be ordinary concentrated sulphuric acid, while a solution of 40 grams of nitrobenzene in 150 grams of slightly fuming sulphuric acid, specific gravity 1.86 to 1.88, constitutes the kathode liquid. The bath is heated by the current. The current density may range from two to six amperes per sq. dm. When the reaction is really under way the temperature should not fall below 80° and should not exceed 120°. To prevent too rapid rise in the resistance of the bath, carefully add, from time to time, a sodium sulphate solution to the anode acid. The latter begins to fume, due to the entrance of HSO_4 ions.

Complete reduction will follow, even if the current is but 20 per cent. of that calculated. At the conclusion of the experiment allow the kathode liquid to cool, then pour it into three times its volume of water and filter after it has stood several hours. The filtrate contains the sulphate of aniline and p-amidophenol, which need not be recovered. Extract the filter contents with hot dilute soda, and from the rapidly filtered solution of the sodium sulphonate liberate by immediate acidification with hydrochloric acid the p-amidophenol-sulphonic acid. It separates as a pale violet, shining, crystalline powder which, after washing, is almost pure. The yield equals about 40 per cent. of the theory calculated from the nitrobenzene.

32. OXIDATION OF p-NITROTOLUENE TO p-NITROBENZYL ALCOHOL.

Electrolytic oxygen oxidizes p-nitrotoluene to p-nitrobenzyl alcohol according to the following equation:



Place a cylinder of nickel gauze, or sheet-lead, serving as kathode in a beaker glass. A large platinum anode stands in a tall porous cup. The kathode liquid is sulphuric acid of 1.6 to 1.7 specific gravity, while the anode liquid consists of a solution of 15 grams of p-nitrotoluene in a mixture of 80 grams of glacial acetic acid, 15 grams of sulphuric acid, and 7 grams of water. The whole apparatus should be heated on a water-bath to 100°. The current density at the anode must not exceed 1.5 ampere per sq. dm. Even under these conditions the consumption of the oxygen is incomplete, and at least three times the quantity of current required by theory must be introduced.

There is scarcely any liberation of hydrogen at the kathode, as it is consumed in the reduction of sulphuric acid to sulphur. Distil the dark brown anode liquid with steam. Acetic acid, unaltered p-nitrotoluene, and some p-nitrobenzyl alcohol will be carried over. It will not pay to recover the latter. The contents of the flask, while yet hot, are filtered through a double, wet filter. The residual resin is boiled up twice with water, and the aqueous solutions are then added to the original filtrate. On cooling, crude p-nitrobenzyl alcohol crystallizes in long yellowish-brown needles. On shaking the mother liquor with ether, p-nitrobenzyl alcohol, some p-nitrobenzyl acetic ester, and a slight quantity of a substance dissolving with difficulty, probably the ether of p-nitrobenzyl alcohol, will be extracted. On distilling off the ether and boiling the residue with a little alcohol, only p-nitrobenzyl alcohol and its acetic ester will dissolve. The yield of p-nitrobenzyl alcohol averages about 40 per cent. of the theory, calculated from the nitrotoluene. The crude product is best purified by recrystallization from warm water, with the addition of a little animal charcoal.

33. PREPARATION OF IODOFORM.

Free iodine, acting upon a warm, aqueous, alkaline solution of ethyl alcohol, produces iodoform. Disregarding intermediate products, the course of the reaction may be represented as follows:

$$CH_3CH_2OH + 10I + H_2O = CHI_3 + CO_2 + 7HI.$$

It is, of course, understood that the hydriodic acid unites with the soda present to produce sodium iodide and carbonic acid.

Place in a beaker glass a kathode of nickel wire gauze and a tall porous cup with platinum anode. The kathode liquid is a moderately concentrated soda solution, while the anode liquid is a solution containing 10 to 15 grams of anhydrous soda and 10 grams of potassium iodide in 100 c.c. of water and 20 c.c. of alcohol. The bath is heated to 60° or 70°. The current density at the anode is about one ampere for one sq. dm. At the expiration of two to four hours interrupt the experiment, pour the anode liquid into a beaker glass, and after standing several hours filter out the beautiful, crystalline iodoform, and allow it to dry at the ordinary temperature. The principal secondary product present in the mother liquor is sodium iodate. The current yield is 60 to 70 per cent.

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